High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years

Rodney J. Weber[1*], Hongyu Guo[1], Armistead G. Russell[2], Athanasios Nenes[1,3, 4, 5]

[1] School of Earth and Atmospheric Sciences, Georgia Institute of Technology
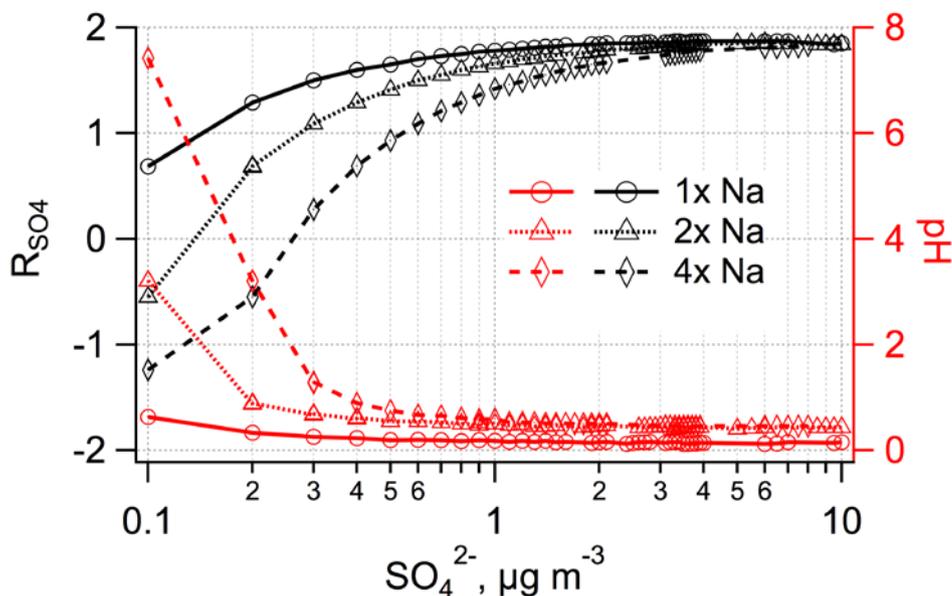
[2] School of Civil & Environmental Engineering, Georgia Institute of Technology

[3] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology

[4] Foundation for Research and Technology – Hellas, Patras, Greece

[5] National Observatory of Athens, Penteli, Greece

*Corresponding author: Rodney Weber, 404-894-1750, rweber@eas.gatech.edu

Extended Data Figure 1: Predicted pH versus sulfate as a function of changes in concentrations of cations other than ammonium. In this sensitivity analyses, NO_3^- and Cl^- are unchanged at 0.08 and 0.02 μg m^{-3}, respectively. Na^+, originally at 0.03 μg m^{-3} is increased by factors of 2 and 4. The plot shows that the decrease in molar ratio (R_{SO4} = $(NH_4^+-NO_3^-)/SO_4^{2-}$) at lower sulfate is related to the other non-volatile cations associating with sulfate. Note that even at significantly higher nonvolatile cation levels internally mixed with fine particles, pH remains below 1 until sulfate drops below roughly 0.3 μg m^{-3}.
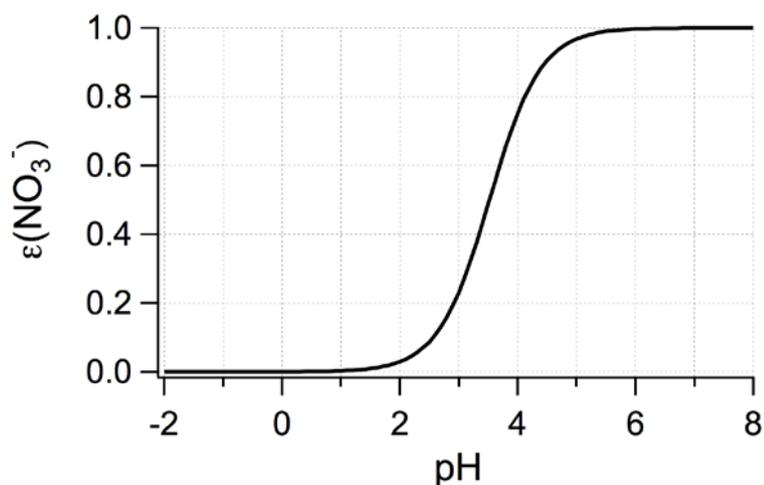
Extended Data Figure 2: Fraction of total nitric acid in the particle phase. The partitioning of nitric acid between the condensed (NO_3^-) and gas phase (HNO_3), ($\varepsilon(NO_3^-)$ = $NO_3^-/(NO_3^- + HNO_3)$) as a function of pH, assuming ideal solutions (activity coefficients of 1) for the average summer conditions during SOAS. The figure shows little nitrate aerosol when pH is below approximately 3, the pH observed in the southeastern US in the past and expected in the future. Lower temperatures shift the curve to the left, accounting for possibly higher $\varepsilon(NO_3^-)$ in colder seasons.

Changes that could impact future pH; Increases in other aerosol cations

The future aerosol pH scenario presented, although highly likely, can be affected by increases in suspended dust from land use changes, drought or other meteorological changes. High concentrations of alkaline mineral dust or transported seasalt components, (carbonates and soluble salts of Ca^{2+}, Mg^{2+}, K^+, Na^+) would force the system to respond differently to sulfate reductions. The dust alkalinity can not only neutralize a larger fraction of acidic sulfate formed in the atmosphere, but also precipitate it out from the aqueous aerosol phase, primarily in the form of gypsum (calcium sulfate). Dust and seasalt alkalinity raises pH at lower sulfate levels (see Extended Data Figure 1) and favors the formation of nitrate, in the forms of Ca^{2+}, Mg^{2+}, K^+ salts and NH_4NO_3. It is also noted that there are instances where the NH_3 mass balance (see Methods) can be more complex, which we have not considered since our interest is on average summer conditions and long-term trends. For example, during cool (winter) or periods of very high relative humidity, significant levels of particle ammonium nitrate could be formed as pH increases due to uptake of substantial quantities of water (e.g., resulting in H^+ dilution). The NH_3 balance would then need to include gas phase nitric acid production and ammonium nitrate deposition. Comprehensive simulations with chemical transport models (CTMs) that include emissions and losses of the major components involved, along with detailed size-resolved particle - gas interactions and aerosol chemistry, would provide greater details. More complex simulations will not change the findings of this work.